

EFFECT OF TEMPERATURE ON MECHANICAL PROPERTIES OF NANOCCLAY REINFORCED POLYMERIC NANOCOMPOSITES – PART I: EXPERIMENTAL RESULTS*

by

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ABSTRACT

In this paper the effect of temperature and nanoclay reinforcement percentage on nanoclay reinforced polymeric nanocomposites is studied. First, polypropylene (PP 3371) resin reinforced with various nanoclay percentages is tested at room, elevated and low temperatures. The tests are conducted on ASTM Type I specimens instrumented with strain gages in an MTS machine equipped with an environmental chamber. Next to ascertain the effect of various PP resins, nanoclay reinforced Borealis and TP 3868 tensile specimens are tested from low to elevated temperatures. In addition nanoclay reinforced epoxy specimens are tested at room temperature. The test results are plotted as stress-strain curves and the mechanical properties of the nanocomposites including Young's modulus, Poisson's ratio, ultimate stress and failure strain are determined. The tensile test results indicate that the Young's modulus of the nanocomposite increases with increasing nanoclay reinforcement percentage. The temperature has even a more significant effect. It was observed that as the temperature decreases the material becomes brittle, has higher stiffness and fails at lower strains. High temperatures have the opposite effect, in that, as the temperature increases the material loses stiffness and becomes more ductile. Temperature and nanoclay reinforcement affect the Poisson's ratio also, but this effect is less significant. In general, as the temperature increases the Poisson's ratio also increases. However, an increase in nanoclay reinforcement generally reduces the Poisson's ratio. It is also noted that the type of resin used may have a significant effect on the mechanical properties of the nanocomposite.

1- INTRODUCTION

Since the 1960's composites have been studied extensively due to their high strength to weight and stiffness to weight ratio and tailorability. Conventional composites consist of a matrix (in many cases a polymeric resin) reinforced with fibers or fabrics. Composites have enjoyed a spectacular success as evidenced by their widespread use in military and commercial aircraft, the automotive industry, sporting goods and even health care products. However, the new trend in structural material design is to make the material multifunctional, i.e. to impart to it thermal, electrical, optical properties in addition to the conventional properties of strength, stiffness and impact and fatigue resistance. One way of making the material multifunctional is with

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nanoadditives. With the recent advances in nanotechnology resin systems have been developed with carbon nanotubes (CNTs), nanoclay particles or flakes, carbon black, etc. to achieve new properties for multifunctionality. In this research, we propose to study the properties of nanoclay reinforced polymers through an experimental and analytical/numerical program.

The main application of using nanoclay additives in polymeric composite systems is to improve their fire retardancy properties, and also reduce toxicity which may ensue as a consequence of fire.

The polymer/nanoclay composites will not be strong enough by themselves to be used as structural materials. Thus, they need to be reinforced with fibers or fabrics. For example the addition of a small amount of nanoclay to composites used in vehicular structures may improve their fire retardancy which is important in protecting the occupants in case of fire.

The composite structures may also be subjected to significant temperature change. For example, all army vehicles are designed to operate in extreme weather conditions from -65°F to 160°F. the temperature variation may not only generate thermal stresses in the structure, but may also significantly affect the mechanical properties of the composite. In light of the facts stated above the goals of this study are: a) to determine the effect of nanoclay reinforcement on the mechanical properties of the nanocomposite b) to ascertain the effect of temperature by varying the temperature from -65°F to 160°F and c) to study the effect of various resins in designing nanoclay reinforced composites.

Even though the literature on nanoclay reinforced composites is extensive, especially the effect of temperature does not appear to have been studied in any meaningful way.

Since the 1980's research in polymer based nanocomposites has increased dramatically with the production of nylon-clay nanocomposites by Toyota [1,2] and their actual or potential applications in diverse areas, such as aerospace components, automotive structures, military equipment, etc.

The improvement of the material properties in nylon/clay nanocomposites was demonstrated by the Toyota research group [3]. Also many researchers investigated numerous other polymers. Some of the polymers include polypropylene [4-18], polyethylene [19-22], polystyrene [23-26], poly(ethylene oxide) [27-30], polycaprolactone [31,32], polyimides [33-37], polycarbonate [38,39] and epoxy resin [40-44].

The use of nanoscale fillers in polymers has provided an opportunity to design new materials with significantly improved performance and multifunctionality. Ongoing research and studies have shown that, in general, polymer based nanocomposites exhibit great improvement in mechanical properties such as strength and stiffness compared to pure polymers with the addition of minimal amount of nanosize clay particles [45-51].

Even though there are numerous studies on the processing and characterization of nanoclay reinforced polymers, here we focus on experimental studies dealing with mechanical properties most relevant to our research.

Wu [52] performed tensile testing on low nanoparticles loaded polymer composites at room temperature and determined the effect of nanoparticles on stiffness, strength and toughness. Simultaneous improvement in Young's modulus, strength and elongation was observed. Sharma [53] measured mechanical properties such as tensile strength, tensile modulus and elongation at break in addition to studying the effects of organically modified clay on the physical, thermal and morphological properties of nanocomposites. Thermal and mechanical test results showed that the interaction of polymer and clay in nanocomposites has high effect on mechanical and thermal properties because of the favorable interface of nanoclay and matrix. Galgali [54] worked on the effect of clay orientation on the tensile modulus of polypropylene nanoclay composites and the relationship between clay orientation and shear rate. Bureau [55] and Drozdov [56] performed similar studies on tensile testing of polypropylene-clay nanocomposites. Bureau used a polypropylene matrix with organo-modified clays. The nanocomposites showed significant improvement in Young's modulus and yield stress. Drozdov performed also tensile tests with different strain rates, creep tests with different stresses and relaxation tests at different strains at room temperature. Test results showed the effect of nanoclay reinforcement on mechanical properties and creep resistance. Clay types can have critical effect on the physical properties of the nanocomposites. To understand the effect of different clays, polypropylenes and preparation methods, Dong [57] performed tensile tests with PP/organoclay nanocomposites which were prepared by using three types of organomodified montmorillonite clay and three grades of PP. The results showed that the PP grade plays the most significant role in the overall mechanical properties and clay content is the second most important factor. Santos [58] optimized the mechanical properties of polypropylene-clay nanocomposites with combination of two different modified clays. Tensile test results showed that the combination of two different clays caused an increase in flexural modulus and higher impact strength.

Beside studies on polypropylene/clay nanocomposites, there are several studies on epoxy/clay nanocomposites. Yasmin [59] studied the mechanical and thermal behavior of epoxy/clay nanocomposites. Test results showed that the elastic modulus and storage modulus were improved and the thermal expansion coefficient was reduced by the addition of clay particles. Sarathi [60] studied the thermal, mechanical and electrical properties of epoxy/clay nanocomposites.

Saber-Samandari [61] manufactured clay/epoxy nanocomposites and performed several experiments including different types of clay with various processing methods such as different centrifuge rotor speeds and curing temperature. The elastic modulus of epoxy-clay nanocomposites increased with the amount of clay up to a maximum of 6%. The tensile strength and energy to failure increased with clay percentage of up to 10%. Zhao [62] focused on the

toughening mechanism of epoxy resin mixed with micro/nano particles and studied the effects of particle size on the maximum stress. The critical particle size for the material system was determined to be 0.95 μ m. Thus it was deduced that particle size should not be more than 0.95 μ m to reduce stress concentrations in the material.

As to the effect of temperature, almost all studies deal with the curing temperature.

In this paper we present extensive experimental results on the mechanical properties of nanoclay reinforced polymers, specifically three grades of polypropylene and epoxy. The effect of nanoclay reinforcement percentage and temperature on the mechanical properties is studied in detail. Even though we performed theoretical and numerical studies to predict the experimental data, those results are presented in the subsequent paper labeled Part 2: Theoretical and Numerical Results.

2- EXPERIMENTAL STUDY ON POLYMER/NANOCLAY COMPOSITES

2.1- The Specimens and Testing Procedure

The nanoclay reinforced PP and epoxy specimens used for tensile testing were Type I ASTM standard dog-bone specimens. Novus Technologies Corporation, manufactured the nanoclay reinforced polypropylene (PP) and epoxy specimens (ASTM D638-08) using injection molding. The main resins were PP 3371 and epoxy with 0%, 0.2%, 1%, 3%, 6% and 10% nanoclay reinforcement by weight. Also additional specimens using two different PP resins, namely Borealis and Total Petrochemical 3868 manufactured with 3% nanoclay reinforcement were tested to ascertain the effect of resin on the mechanical properties. The specimens were instrumented with strain gages and tensile tested in an MTS machine at a crosshead speed of 5mm/min except for epoxy specimens which were tested at 2mm/min.

Both loading and elongation histories were recorded through a National Instruments (NI)-DAQ based Lab View data acquisition system. Then the stress-strain curves were obtained using the time-history reading from load-cell and crosshead motion. The tensile tests were performed on all specimens at room temperature (RT), -65°F, -4°F, 120°F and 160°F, except for epoxy specimens which were tested at room temperature only. For each case 5 to 10 specimens were used and the stress-strain curves obtained were plotted. A typical specimen instrumented with strain gages is shown in Figure 2.1.

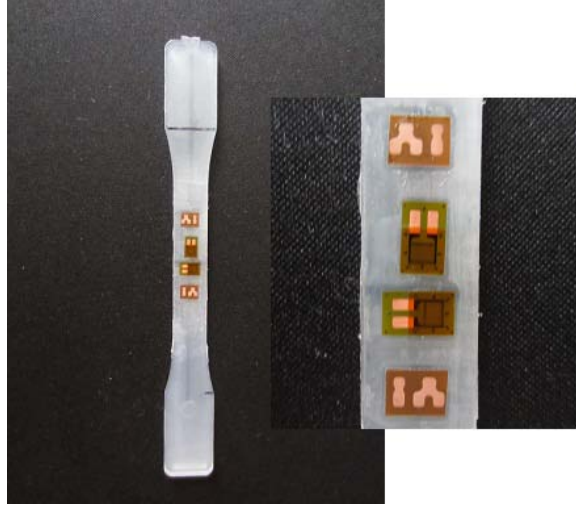


Figure 2.1 PP 3371 specimen with attached strain gages

2.2- The Experimental Results

Extensive results were obtained for the main resin PP 3371 which was reinforced with various nanoclay percentages (0.2%, 1%, 3%, 6% and 10% by weight) at -65°F, -4°F, RT, 120°F and 160°F. Two additional grades of PP, namely, Borealis and TP 3868, reinforced with 3% nanoclay were also tested at the same temperatures. However, the epoxy specimens with 1%, 3%, 6% and 10% nanoclay reinforcement were tested at room temperature only. The experimental results are organized in a manner to showcase the effect of nanoclay reinforcement, temperature and PP grades on the mechanical properties. The results for epoxy are presented separately. A more presentation of the experimental results can be found in the doctoral dissertation of the first author [63].

2.2.1 Effect of nanoclay reinforcement

To ascertain the effect of nanoclay percentage on the mechanical properties, first at each temperature we compare the stress-strain curves obtained for various nanoclay reinforcement percentage. Figures 2.2-2.6 show the results at RT, 120°F, 160°F, -4°F and -65°F respectively.

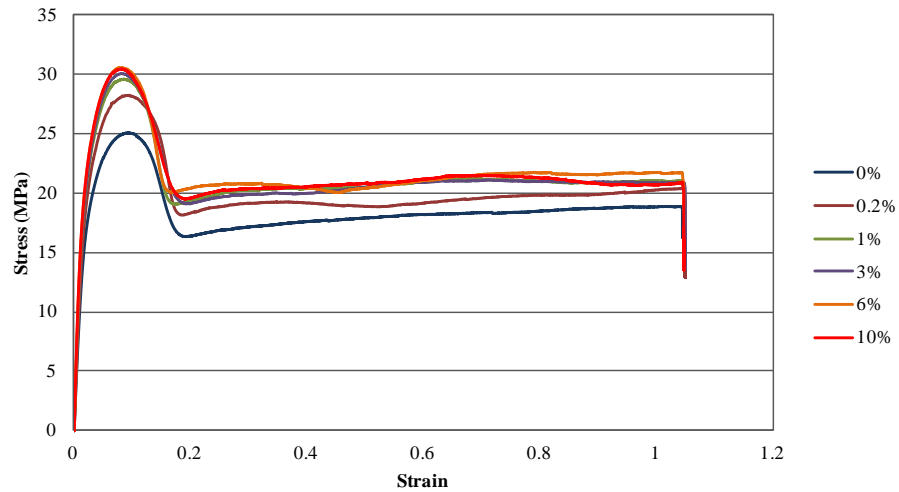


Figure 2.2 Comparison of stress-strain curves of PP 3371 specimens with 0%, 0.2%, 1%, 3%, 6% and 10% nanoclay reinforcement at room temperature

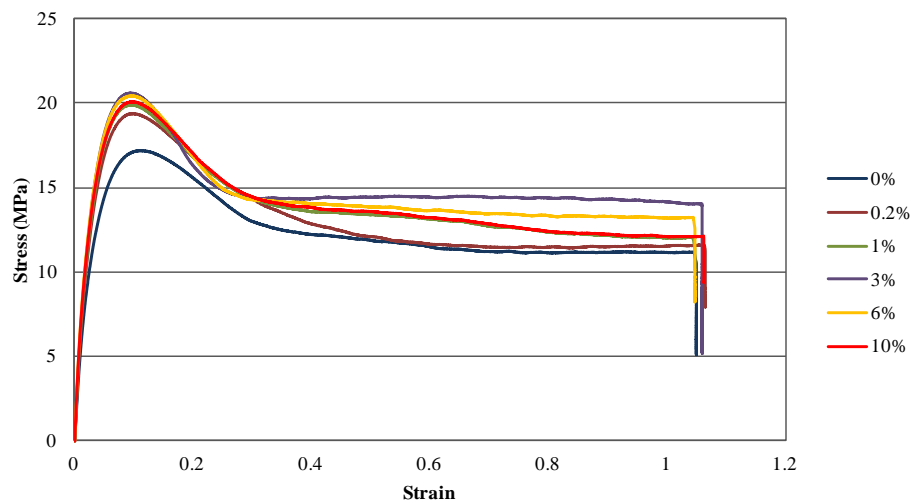


Figure 2.3 Comparison of stress-strain curves of PP 3371 specimens with 0%, 0.2%, 1%, 3%, 6% and 10% nanoclay reinforcement at 120°F (49°C)

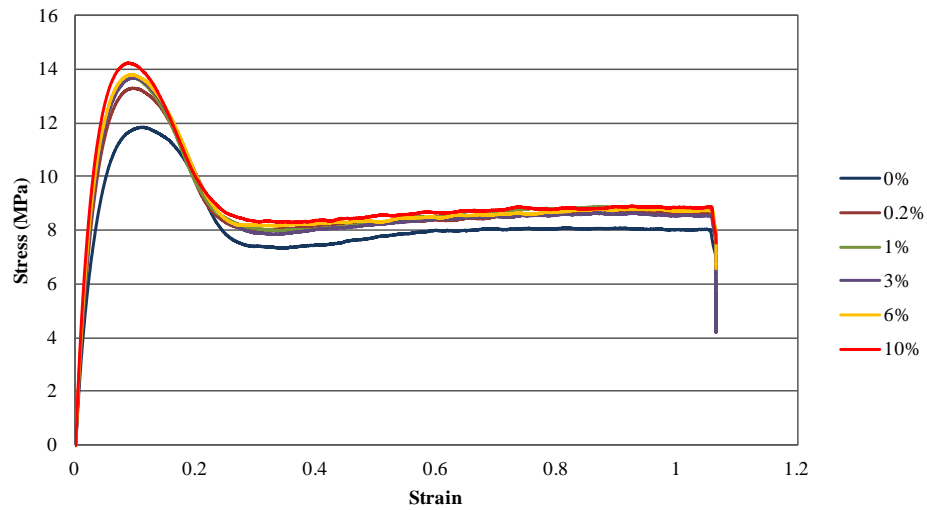


Figure 2.4 Comparison of stress-strain curves of PP 3371 specimens with 0%, 0.2%, 1%, 3%, 6% and 10% nanoclay reinforcement at 160°F (71°C)

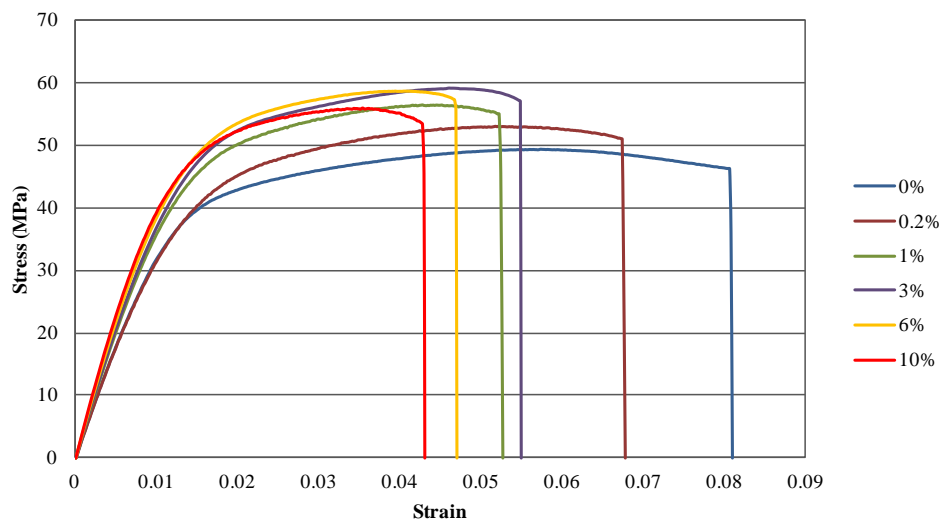


Figure 2.5 Comparison of stress-strain curves of PP 3371 specimens with 0%, 0.2%, 1%, 3%, 6% and 10% nanoclay reinforcement at -4°F (-20°C)

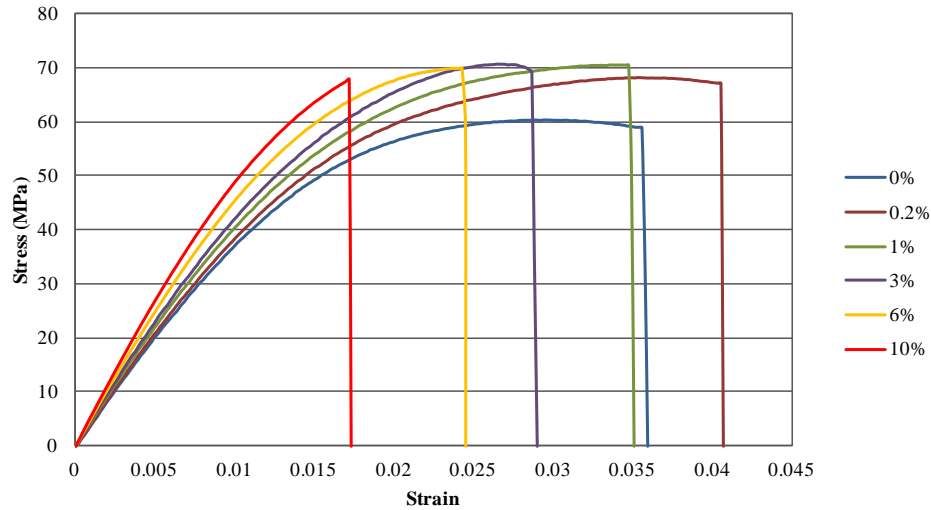


Figure 2.6 Comparison of stress-strain curves of PP 3371 specimens with 0%, 0.2%, 1%, 3%, 6% and 10% nanoclay reinforcement at -65°F (-54°C)

The results shown in Figure 2.2-2.6 can also be replotted as a function of reinforcement percentage for each temperature (Figure 2.7).

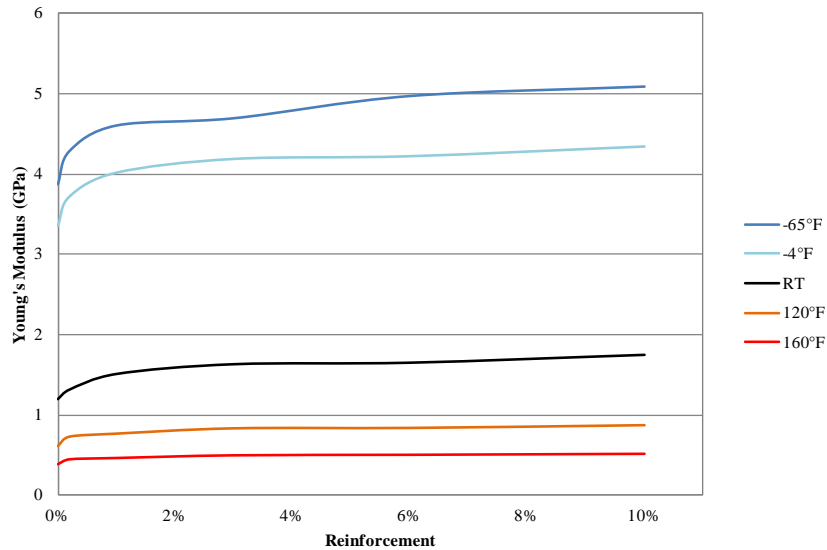


Figure 2.7 Variation of Young's modulus with nanoclay reinforcement percentage at various test temperatures

Also the Poisson's ratios obtained from the strain gage readings are plotted as a function of nanoclay reinforcement percentage for each temperature and shown in Figure 2.8.

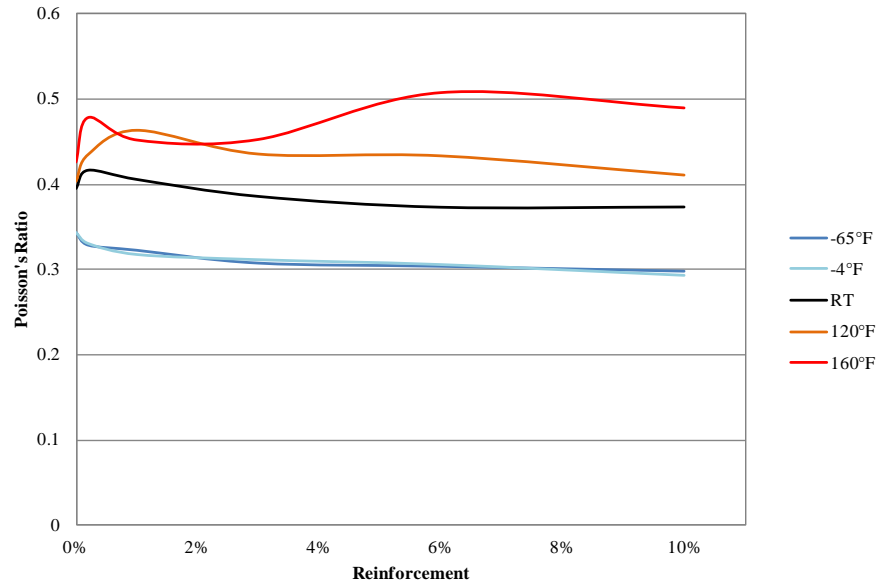


Figure 2.8 Variation of Poisson's ratio with nanoclay reinforcement percentage at various test temperatures

All the average mechanical properties obtained from the above curves at each temperature and reinforcement percentage are summarized in Table 1.

Table 1. Average mechanical properties of PP 3371 specimens with 0%, 0.2%, 1%, 3%, 6% and 10% nanoclay reinforcement at -65°F (-54°C), -4°F (-20°C), room temperature (RT), 120°F (49°C) and 160°F (71°C)

PP 3371	Temperature	Young's Modulus (GPa)	Poisson's Ratio	Ultimate Stress (MPa)	Strain at Ultimate Stress	Failure or End of Test Strain
0%	-65°F (-54°C)	3.866	0.3429	63.9034	0.0327	0.0357
	-4 °F (-20°C)	3.346	0.3438	50.607	0.0517	0.0642
	Room Temp.	1.200	0.3947	25.122	0.0745	1.0233
	120 °F (49°C)	0.616	0.4038	17.166	0.0919	1.0021
	160 °F (71°C)	0.392	0.4256	11.730	0.0819	1.0360
0.2%	-65°F (-54°C)	4.284	0.3283	68.5570	0.0325	0.0372
	-4 °F (-20°C)	3.713	0.3307	53.8378	0.0491	0.0619
	Room Temp.	1.317	0.4167	27.826	0.0668	1.0258
	120 °F (49°C)	0.728	0.4350	19.087	0.0788	1.0355
	160 °F (71°C)	0.449	0.4782	12.997	0.0725	1.0308
1%	-65°F (-54°C)	4.603	0.3193	65.1837	0.0254	0.0259
	-4 °F (-20°C)	4.008	0.3156	56.3626	0.0431	0.0523
	Room Temp.	1.508	0.4056	29.277	0.0661	1.0268
	120 °F (49°C)	0.765	0.4631	19.583	0.0772	1.0345
	160 °F (71°C)	0.465	0.4715	13.303	0.0732	1.0341
3%	-65°F (-54°C)	4.694	0.3076	67.0177	0.0247	0.0272
	-4 °F (-20°C)	4.179	0.3114	55.5831	0.0433	0.0518
	Room Temp.	1.628	0.3852	29.900	0.0653	1.0397
	120 °F (49°C)	0.828	0.4355	19.954	0.0789	1.0336
	160 °F (71°C)	0.497	0.4523	13.567	0.0713	1.0354
6%	-65°F (-54°C)	4.973	0.3039	61.5911	0.0203	0.0203
	-4 °F (-20°C)	4.212	0.3056	52.3178	0.0409	0.0471
	Room Temp.	1.646	0.3722	30.009	0.0659	1.0332
	120 °F (49°C)	0.833	0.4334	19.863	0.0759	1.0248
	160 °F (71°C)	0.503	0.5077	13.396	0.0774	1.0374
10%	-65°F (-54°C)	5.092	0.2983	60.2389	0.0192	0.0194
	-4 °F (-20°C)	4.333	0.2928	54.0557	0.0367	0.0427
	Room Temp.	1.742	0.3725	30.073	0.0658	1.0331
	120 °F (49°C)	0.866	0.4111	19.981	0.0759	1.0353
	160 °F (71°C)	0.515	0.4896	13.431	0.0791	1.0338

The results displayed and tabulated above clearly demonstrate the effect of nanoclay reinforcement on the mechanical properties. First, it can be seen in Figures 2.2-2.6 that at any temperature as the reinforcement percentage increases the initial slope of the stress-strain curve also increases, meaning that the material becomes stiffer and the Young's modulus has a higher value. This effect can also be deduced from the results given in Table 1. Second, again at each temperature as the reinforcement percentage increases, in general, the ultimate stress or strength of the nanocomposite also increases. The increase is more pronounced at lower percentages and

beyond 1% it is not significant. Adding too much nanoclay to the polymer does not result in significantly higher strength. It was observed that at room and the higher temperatures the specimens did not fail at 100% strain when testing stopped. However at the lower temperatures i.e., at -4°F and -65°F the specimens failed at relatively low strains and for those cases in general a higher reinforcement percentage meant a lower failure strain.

It must be noted that the test results for the Poisson's ratio showed more variation, especially at higher temperatures. Even though it is difficult to identify a definite trend with the reinforcement percentage, one can tentatively state that the Poisson's ratio in general decreases with increasing reinforcement percentage, except at high temperatures. This may be due to the fact that at the higher temperatures PP softens and the Poisson's ratio measurements become less reliable.

2.2.2 Effect of nanoclay temperature

The experimental results presented earlier can be displayed differently to show the effect of temperature on the mechanical properties of the material. Figures 2.9-2.14 show the stress-strain curves for the temperature range considered at a given reinforcement percentage.

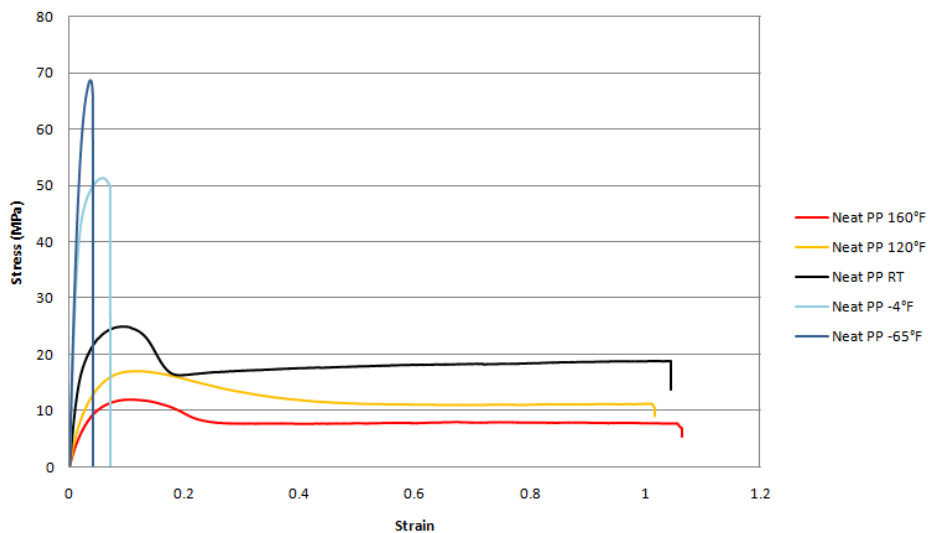


Figure 2.9 Comparison of stress-strain curves of neat PP 3371 specimens obtained at -65°F (-54°C), -4°F (-20°C), RT, 120°F (49°C) and 160°F (71°C)

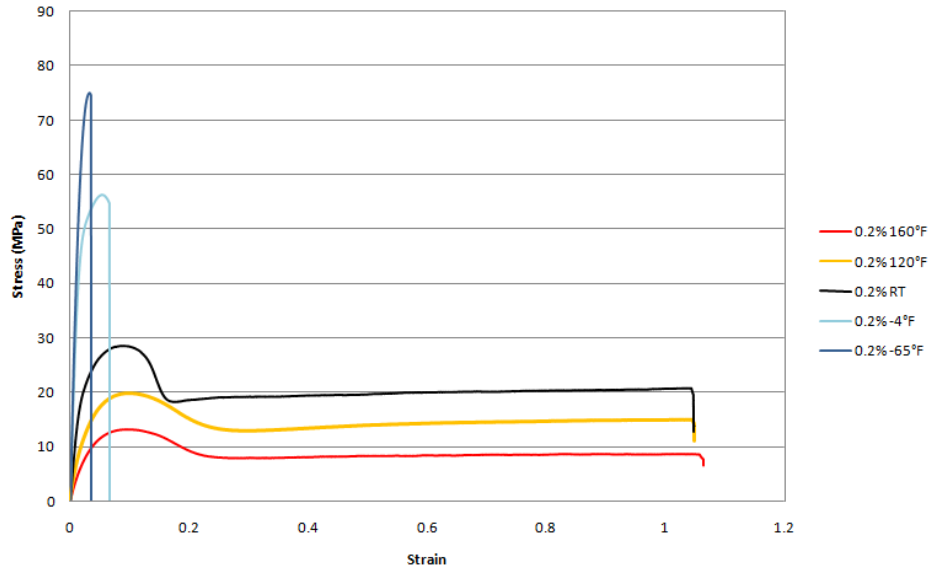


Figure 2.10 Comparison of stress-strain curves of PP 3371 specimens with 0.2% nanoclay reinforcement obtained at -65°F (-54°C), -4°F (-20°C), RT, 120°F (49°C) and 160°F (71°C)

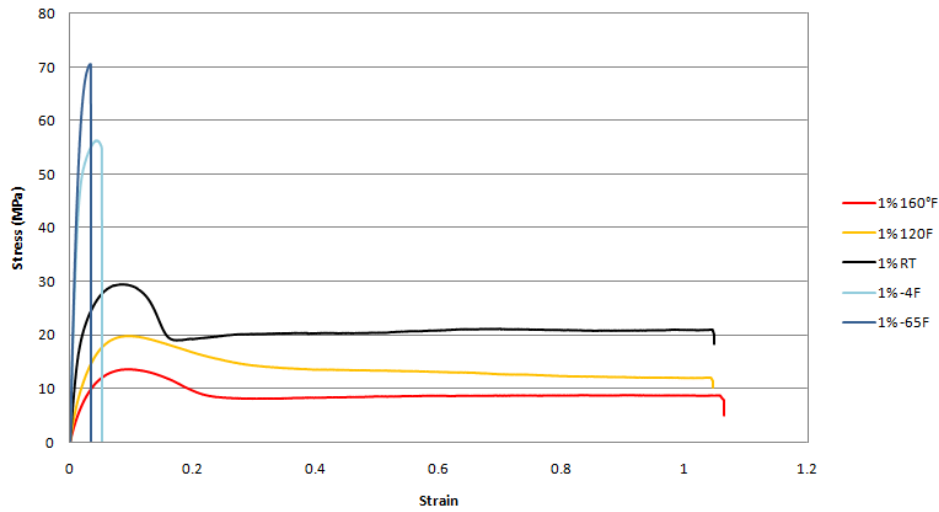


Figure 2.11 Comparison of stress-strain curves of PP 3371 specimens with 1% nanoclay reinforcement obtained at -65°F (-54°C), -4°F (-20°C), RT, 120°F (49°C) and 160°F (71°C)

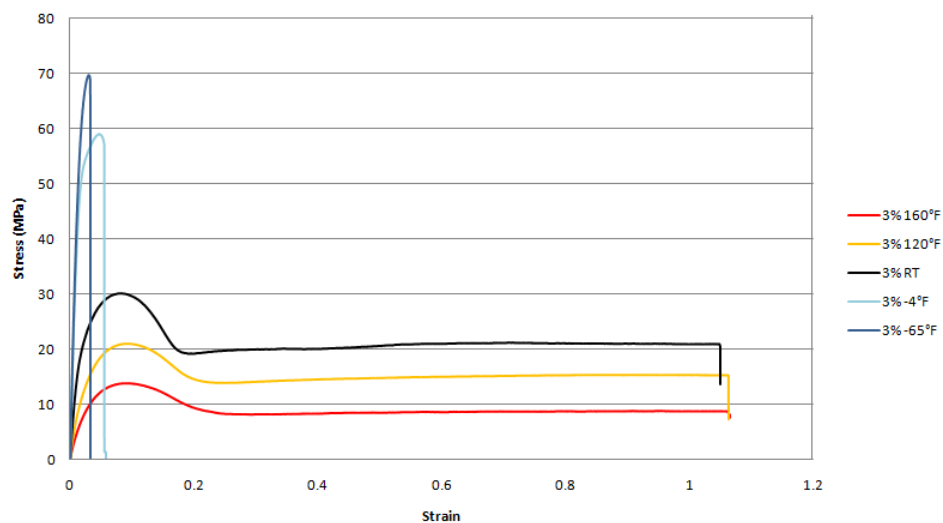


Figure 2.12 Comparison of stress-strain curves of PP 3371 specimens with 3% nanoclay reinforcement obtained at -65°F (-54°C), -4°F (-20°C), RT, 120°F (49°C) and 160°F (71°C)

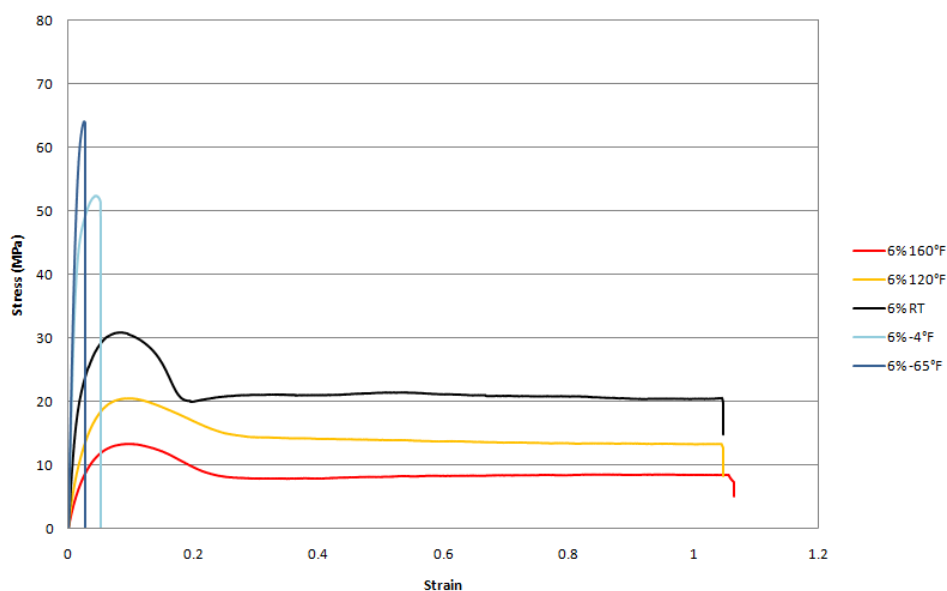


Figure 2.13 Comparison of stress-strain curves of PP 3371 specimens with 6% nanoclay reinforcement obtained at -65°F (-54°C), -4°F (-20°C), RT, 120°F (49°C) and 160°F (71°C)

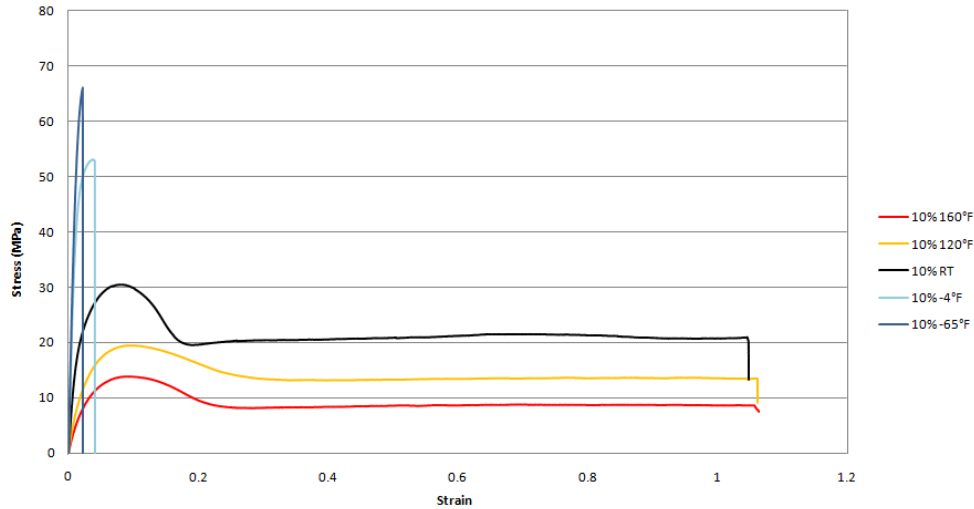


Figure 2.14 Comparison of stress-strain curves of PP 3371 specimens with 10% nanoclay reinforcement obtained at -65°F (-54°C), -4°F (-20°C), RT, 120°F (49°C) and 160°F (71°C)

The variation of Young's modulus with temperature for each reinforcement percentage is shown in Figure 2.15.

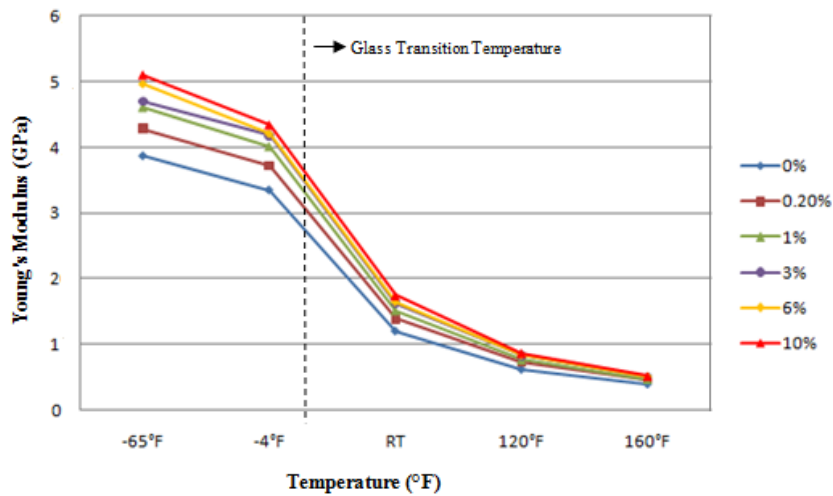


Figure 2.15 Variation of Young's modulus with temperature

Similarly, the variation of Poisson's ratio with temperature for each reinforcement percentage is depicted in Figure 2.16.

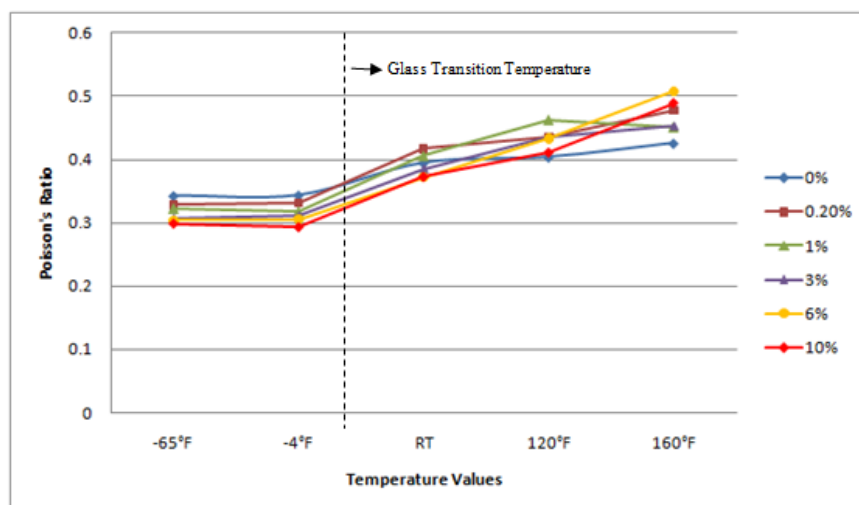


Figure 2.16 Variation of Poisson's ratio with temperature

The results shown in the above figures and Table 1 indicate that temperature has not only a significant effect on the mechanical properties of the nanocomposite but may also change its behavior drastically. The results in Figure 2.15 clearly show the effect of temperature on the Young's modulus. For all reinforcement percentages, the Young's modulus is reduced significantly as the temperature increases. It is also observed that between -4°F and RT, the change in Young's modulus is drastic. This is due to the fact that, the glass transition temperature (T_g) of PP is around 14°F and as the temperature increases beyond 14°F PP loses its glassy state and becomes more ductile resulting in a drastically lower Young's modulus.

Temperature has also a very significant effect on the strength of the composite. At lower temperatures the material has higher strength compared to higher temperatures. In other words, as the temperature increases the material becomes softer and loses strength. The most drastic effect of the temperature change is on the failure behavior of the material. At room and higher temperatures, the composite is basically ductile and the failure strain is higher than 100%. However, at lower temperatures the material becomes very brittle and fails at relatively low strains.

The effect of temperature on the Poisson's ratio is less pronounced. In general the Poisson's ratio increases with increasing temperature with most of the increase occurring after the glass transition temperature.

2.2.3 Effect of PP grade on the mechanical properties of the composite

Three grades of PP, namely, PP 3371, Borealis and TP 3868 were tested at various temperatures to elicit the effect of different resins. The nanoclay reinforcement percentage was kept constant at 3%. The stress-strain curves for PP 3371 with 3% nanoclay reinforcement at various temperatures were given in Figure 2.12. The same results for Borealis and TP 3868 are shown

below in Figures 2.17 and 2.18 respectively. The comparison of the stress-strain curves for the 3 PP grades at room temperature is shown in Figure 2.19. Finally, the mechanical properties calculated from the test results are summarized in Table 2 for all three grades of PP.

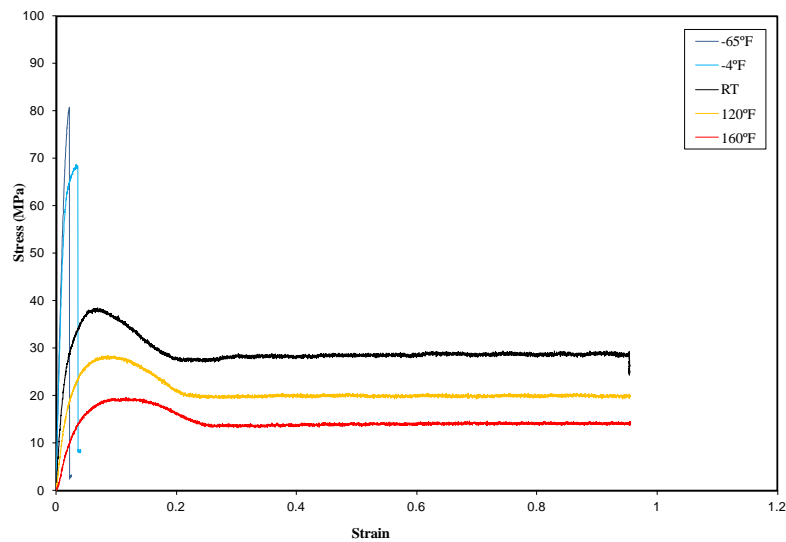


Figure 2.17 Comparison of stress-strain curves of Borealis specimens with 3% nanoclay reinforcement at various temperatures

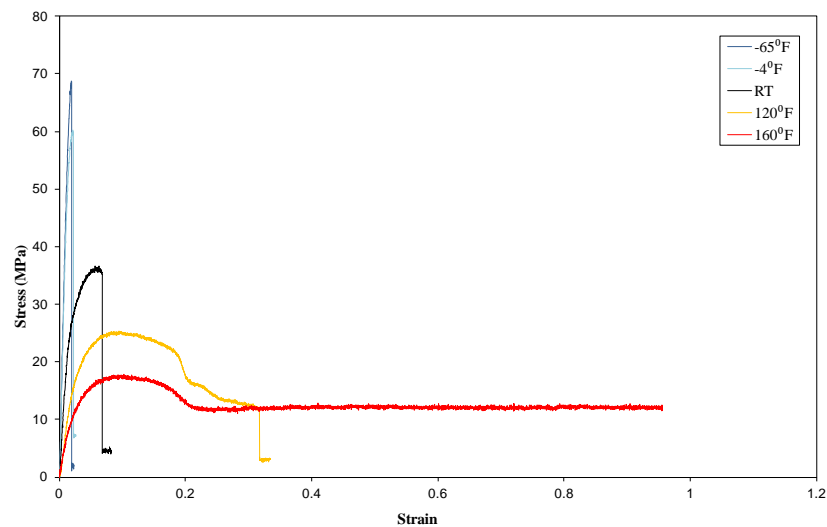


Figure 2.18 Comparison of stress-strain curves of TP 3868 specimens with 3% nanoclay reinforcement at various temperatures

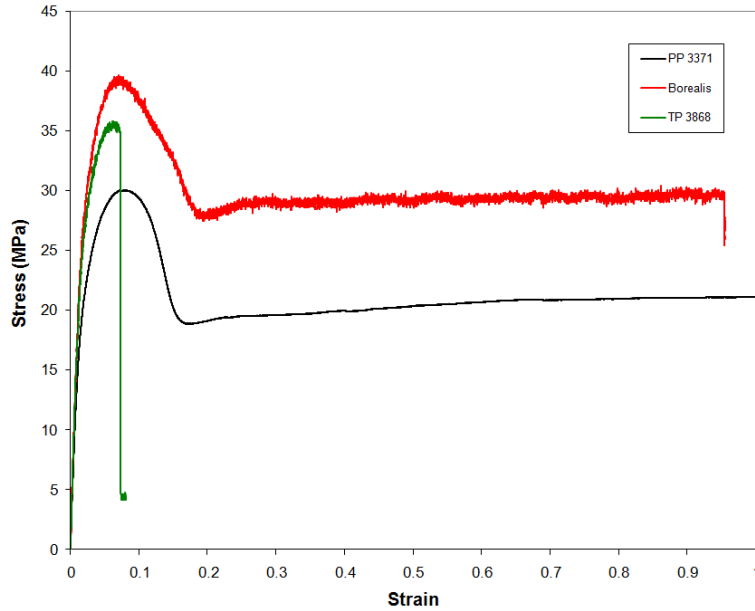


Figure 2.19 Comparison of stress-strain curves of PP 3371, Borealis and TP 3868 specimens with 3% nanoclay reinforcement at room temperature

Table 2. Comparison of average mechanical properties of PP 3371, Borealis and TP 3868 reinforced with 3% nanoclay at -65°F (-54°C), -4°F (-20°C), room temperature, 120°F (49°C) and 160°F (71°C)

PP Grade	Temperature	Young's Modulus (GPa)	Ultimate Stress (MPa)	Strain at Ultimate Stress	End of Test or Failure Strain
PP 3371	-65°F (-54°C)	4.694	67.018	0.025	0.027
	-4°F (-20°C)	4.179	55.583	0.043	0.052
	RT	1.628	29.90	0.065	1.039
	120°F (49°C)	0.828	19.954	0.079	1.034
	160°F (71°C)	0.497	13.567	0.071	1.035
Borealis	-65°F (-54°C)	5.704	80.140	0.022	0.022
	-4°F (-20°C)	5.109	67.173	0.033	0.037
	RT	1.965	38.944	0.073	0.954
	120°F (49°C)	1.020	27.914	0.091	0.951
	160°F (71°C)	0.569	19.405	0.106	0.951
TP 3868	-65°F (-54°C)	4.858	64.157	0.017	0.017
	-4°F (-20°C)	4.423	58.192	0.022	0.022
	RT	1.875	34.783	0.061	0.071
	120°F (49°C)	0.830	25.099	0.093	0.526
	160°F (71°C)	0.587	17.671	0.099	0.945

The results are shown in Figures 2.17-2.19 and summarized in Table 2 indicate that the mechanical behavior of Borealis is very similar to that of PP 3371. Both are very ductile at room temperature and become brittle at lower temperatures. However, TP 3868 is much less ductile when compared to PP 3371 and Borealis (Figure 2.19) and more brittle at lower temperatures

(Table 2.) As was discussed previously, temperature greatly affects the behavior of the resins, making them more ductile at higher temperatures and brittle at lower temperatures. The effect of temperature on Young's modulus and strength is also similar to that reported before, that is, they increase with decreasing temperature.

2.2.4 Results for epoxy based nanoclay reinforced specimens

Finally, epoxy (EPON 828) specimens with 0%, 1%, 3%, 6% and 10% nanoclay reinforcement were subjected to tensile testing at room temperature. The specimens were instrumented with an extensometer and strain gages to enable us to obtain the Poisson's ratios also. A summary of the stress-strain curves showing the effect of reinforcement percentage is given in Figure 2.20.

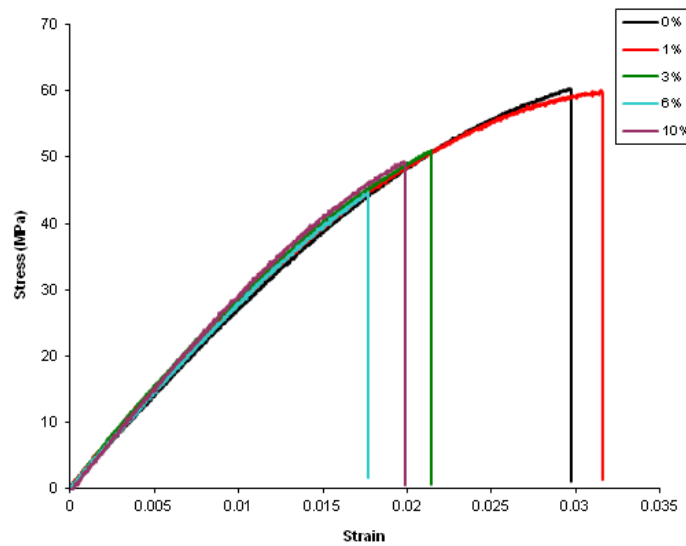


Figure 2.20 Comparison of stress-strain curves of EPON 828 epoxy specimens with various nanoclay reinforcement percentages

The average mechanical properties calculated from the test results are also shown in Table 3.

Table 3. Average material properties of EPON 828 epoxy specimens with 0%, 1%, 3%, 6% and 10% nanoclay reinforcement at room temperature

EPON 828	Young's Modulus (GPa) - Extensometer	Maximum Strength (MPa)	Failure Strain (ϵ_f)	Young's Modulus (GPa) (Manufacturer)	Poisson's Ratio (ν_{12})
0%	2.8177	59.06	0.032	2.758	0.3105
1%	2.9127	58.84	0.032	-	0.3238
3%	2.9840	50.99	0.022	-	0.3288
6%	3.0965	38.97	0.014	-	0.3340
10%	3.3427	37.74	0.014	-	0.3348

Even though the epoxy results presented here are much less extensive than those obtained for PP resin, nevertheless they allow us to identify some trends and draw some conclusions. First, it is noted that the epoxy resin itself has a much lower failure strain compared to PP and the addition of nanoclay in general reduces the failure strain. Also the effect of nanoclay on the Young's modulus is less significant. For example adding 3% of nanoclay to PP at room temperature increased the corresponding Young's modulus by approximately 36%, whereas an addition of similar amount to epoxy increases its Young's modulus by 6% only (Table 3.). However the effect on the strength of the epoxy based composite is deleterious as the strength decreases with increasing amount of nanoclay. Addition of 3% nanoclay decreases the strength of the epoxy by approximately 14% (Table 3.) whereas the same amount of nanoclay added to PP increases the strength of the PP based composite by 19% (Table 1).

The epoxy stress-strain curves are compared to those obtained for the three PP grades and are shown in Figure 2.21.

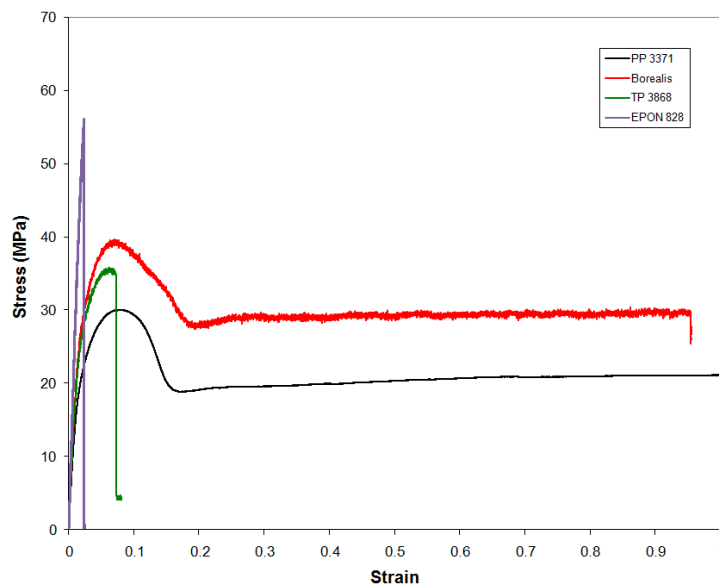


Figure 2.21 Comparison of stress-strain curves of PP 3371, Borealis, TP 3868 and EPON 828 specimens with 3% nanoclay reinforcement at room temperature

The comparison clearly shows that the epoxy based composites are much more brittle, (i.e., they fail at much lower strains compared to PP), are stiffer (have higher Young's modulus) and have comparable strength to PP based composites.

3. DISCUSSION AND RESULTS

In this study three grades of PP, namely, PP 3371, Borealis and TP 3868 and epoxy were reinforced with nanoclay and tensile tested at various temperatures. The effects of nanoclay reinforcement and temperature on the mechanical properties of the resulting nanocomposites

were studied in detail. The tensile test program yielded a wealth of data which were analyzed extensively. Then to predict the values of Young's modulus and Poisson's ratio obtained experimentally theoretical and numerical models were developed and compared with the experimental results. Due to the length of the current manuscript, the analytical and numerical results are presented as Part II in a subsequent paper. The experimental results are presented in graphical and tabular form as needed. The results are organized to illustrate the effect of nanoclay reinforcement, temperature and the PP grades used as resins. In addition, less extensive results are presented for a nanoclay reinforced epoxy composite.

Figures 2.2-2.6 show the stress-strain curves for various nanoclay reinforcement percentages at each test temperature. As discussed earlier, it is seen that at each temperature as the percentage of nanoclay increases, in general the material becomes stiffer (higher Young's modulus), stronger (higher strength) and less ductile. Even though the loss of ductility with increasing nanoclay reinforcement is not readily apparent at room and higher temperatures (because the specimens did not fail at 100% strain), the loss of ductility is readily visible at lower temperatures (see Figures 2.5 and 2.6). The effect of nanoclay reinforcement on the Young's modulus can clearly be observed in Figure 2.7. For example adding 10% nanoclay to PP will increase its Young's modulus from 30% to 45% depending on temperature. The effect of nanoclay reinforcement percentage on the Poisson's is not very clear. At lower temperatures, the Poisson's ratio decreases with increasing nanoclay percentage. However at room and higher temperatures the trend is not clear and especially at high temperatures as the material softens the strain gage results may not be reliable. The stress curves shown in Figures 2.9-2.14 basically depict the effect of temperature at each reinforcement percentage. The most eye-catching feature of the curves is the drastic reduction in the failure strain as the temperature is reduced from 160°F to -65°F. At low temperatures the material becomes brittle, stiffer (i.e., the Young's modulus increases) and the strength also improves significantly. Higher temperatures have the opposite effect, that is the material becomes more ductile and the strength and Young's modulus are reduced. Figures 2.14 and 2.15 show the variation of Young's modulus and Poisson's ratio with temperature for the various reinforcement percentages. At each reinforcement percentage the Young's modulus decreases with increasing temperature. The most decrease occurs between -4°F and RT, because in that range the glass transition temperature of PP is crossed and the material changes from a glassy state to a rubbery state. The change in the Poisson's ratio with temperature is not as pronounced, but in general we can state that the Poisson's ratio increases with increasing temperature. The results related to the different PP grades are given in Figures 2.17-2.19. Figure 2.17 shows the stress-strain curves for Borealis resin at various temperatures. It is seen that the behavior of the resin is very similar to that of PP 3371, with increasing ductility at higher temperature and brittle failure at lower temperatures. On the other hand TP 3868, whose stress-strain curves are depicted in Figure 2.18, is less ductile than both PP 3371 and Borealis. This fact can also clearly be seen when comparing the behavior of all three resins (Figure 2.19). The comparison of the mechanical properties obtained is summarized in Table 2.

Finally, the stress-strain curves obtained for the epoxy specimens are shown in Figure 2.20 and the calculated average mechanical properties summarized in Table 3. In general as the percentage of nanoclay increases the Young's modulus increases and failure strain decreases. In comparing the epoxy results with those obtained for the three grades of PP specimens (Figure 2.21), one can observe that the behavior of epoxy specimens is drastically different than the PP specimens. While the nanoclay reinforced PP specimens exhibit by-and-large relatively ductile behavior, the epoxy specimens clearly show more brittle behavior in comparison.

4. CONCLUSIONS

Based on the results in the figures, tables and the discussion above, we may draw the following conclusions:

- a. Nanoclay reinforcement leads to an increase in Young's modulus and strength and a decrease in the Poisson's ratio and failure strain
- b. An increase in temperature makes the material more ductile leading to lower Young's modulus and strength. On the other hand, lower temperatures result in a stiffer and more brittle material that is a composite with higher Young's modulus and smaller failure strain. In general, the Poisson's ratio increases with increasing temperature
- c. The effect of temperature on the mechanical properties and general behavior of the material is more significant than the effect of nanoclay reinforcement
- d. The grade of PP resin used may also have significant effect on the mechanical properties of the resulting composite
- e. When compared to PP nanoclay reinforced epoxy composites are stiffer, more brittle but show similar strength.

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References

- [1] Kojima Y., Usuki A., Kawasumi M., Okada A., Fukushima Y., Kurauchi T., et al. *Mechanical properties of nylon 6-clay hybrid*, J. Mater Res., Volume 8, 1993, Pages 1185-1189.
- [2] Kojima Y., Usuki A., Kawasumi M., Okada A., Fukushima Y., Kurauchi T., et al. *Sorption of water in nylon 6-clay hybrid*, J. Appl. Polym. Sci., Volume 49, 1993, Pages 1259-1264.
- [3] A. Okada, Y. Fukushima, S. Inagaki, A. Usuki, S. Sugiyama, T. Kurashi, O. Kamigaito., U.S. **4,739,007** (1998).

- [4] Nguyen Q. T., *Process for Improving Exfoliation and Dispersion of Nanoclay Particles into Polymer Matrices Using Supercritical Carbon Dioxide*. PhD. Dissertation , Blacksburg, VA, 2007.
- [5] M. Kato, A. Usuki and A. Okada, Synthesis of polypropylene oligomer - clay intercalation compounds. *J Appl Polym Sci* **66** (1997), pp. 1781.
- [6] M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki and A. Okada Preparation and Mechanical Properties of Polypropylene-Clay Hybrids. *Macromolecules* 30 (1997), pp. 6333.
- [7] N. Hasegawa, M. Kawasumi, M. Kato, A. Usuki and A. Okada, Preparation and mechanical properties of polypropylene-clay hybrids using a maleic anhydride-modified polypropylene oligomer *J Appl Polym Sci* 67 (1998), p. 87.
- [8] X. Liu and Q. Wu, PP/clay nanocomposites prepared by grafting-melt intercalation. *Polymer* 42 (2001), p. 10013.
- [9] P.H. Nam, P. Maiti, M. Okamoto, T. Kotaka, N. Hasegawa and A. Usuki, A hierarchical structure and properties of intercalated polypropylene/clay nanocomposites. *Polymer* 42 (2001), p. 9633.
- [10] Y. Kurokawa, H. Yasuda, M. Kashiwagi and A. Oya, Structure and properties of a montmorillonite/polypropylene nanocomposite. *J Mater Sci Lett* 16 (1997), pp. 1670–1672
- [11] R. Nyden and J.W. Gilman, Molecular dynamics simulations of the thermal degradation of nano-confined polypropylene. *Comput Theor Polym Sci* 7 (1997), pp. 191–198.
- [12] M. Kato, A. Usuki and A. Okada, Synthesis of polypropylene oligomer–clay intercalation compounds. *J Appl Polym Sci* 66 (1997), pp. 1781–1785
- [13] A. Usuki, M. Kato, A. Okada and T. Kurauchi, Synthesis of polypropylene–clay hybrid. *J Appl Polym Sci*, 63 (1997), pp. 137–138.
- [14] M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki and A. Okada, Preparation and mechanical properties of polypropylene–clay hybrids. *Macromolecules* 30 (1997), pp. 6333–6338.
- [15] N. Hasegawa, M. Kawasumi, M. Kato, A. Usuki and A. Okada, Preparation and mechanical properties of polypropylene–clay hybrids using a maleic anhydride-modified polypropylene oligomer. *J Appl Polym Sci* 67 (1998), pp. 87–92.
- [16] A. Oya, Polypropylene–clay nanocomposites. In: T.J. Pinnavaia and G.W. Beall, Editors, *Polymer–clay nanocomposites*, Wiley, London (2000), pp. 151–172.

- [17] N. Hasegawa, H. Okamoto, M. Kato and A. Usuki, Preparation and mechanical properties of polypropylene–clay hybrids based on modified polypropylene and organophilic clay. *J Appl Polym Sci* 78 (2000), pp. 1918–1922.
- [18] M. Zanetti, G. Camino, P. Reichert and R. Mulhaupt, Thermal behaviour of poly(propylene) layered silicate nanocomposites. *Macromol Rapid Commun* 22 (2001), pp. 176–180.
- [19] H.G. Jeon, H.T. Jung, S.W. Lee and S.D. Hudson, Morphology of polymer silicate nanocomposites. High density polyethylene and a nitrile. *Polym Bull* 41 (1998), pp. 107–113.
- [20] J. Heinemann, P. Reichert, R. Thomson and R. Mulhaupt, Polyolefin nanocomposites formed by melt compounding and transition metal catalyzed ethane homo- and copolymerization in the presence of layered silicates. *Macromol Rapid Commun* 20 (1999), pp. 423–430.
- [21] V.P. Privalko, F.J.B. Calleja, D.I. Sukhorukov, E.G. Privalko, R. Walter and K. Friedrich, Composition-dependent properties of polyethylene/Kaolin composites. Part II. Thermoelastic behavior of blow-molded samples. *J Mater Sci* 34 (1999), pp. 497–508.
- [22] J.S. Bergman, H. Chen, E.P. Giannelis, M.G. Thomas and G.W. Coates, Synthesis and characterization of polyolefin-silicate nanocomposites: a catalyst intercalation and in situ polymerization approach. *J Chem Soc Chem Commun* 21 (1999), pp. 2179–2180.
- [23] R. A. Vaia, H. Isii, and E. P. Giannelis, Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melt in layered silicates. *Chem Mater* 5 (1993), pp 1694.
- [24] R. A. Vaia, K. D. Jandt, J. K. Edward, and E. P. Giannelis, Kinetics of Polymer Melt Intercalation. *Macromolecules* 28 (1995), pp. 8080.
- [25] A. Moet and A. Akelah, Polymer-clay nanocomposites: polystyrene grafted onto montmorillonite interlayers. *Mater Lett.* 18 (1993), pp. 97.
- [26] N. Hasegawa, H. Okamoto, M. Kawasumi, and A. Usuki, Preparation and mechanical properties of polystyrene-clay hybrids. *J. Appl. Polym. Sci.*, 74 (1999), pp. 3359.
- [27] P. B. Messersmith and E. P. Giannelis, Synthesis and barrier properties of poly(-caprolactone)-layered silicate nanocomposites. *J. Polym. Sci. Part A: Polym. Chem.*, 33 (1995), pp. 1047.
- [28] E. Hackett, E. Manias and E.P. Giannelis, Computer simulation studies of PEO/layered silicate nanocomposites. *Chem Mater* 12 (2000), pp. 2161–2167.
- [29] V. Kупpa and E. Manias, Computer simulation of PEO/layered-silicate nanocomposites: 2. Lithium dynamics in PEO/Li⁺ montmorillonite intercalates. *Chem Mater* 14 (2002), pp. 2171–2175.

- [30] P. Aranda and E. Ruiz-Hitzky, Poly(ethylene oxide)-silicate intercalation materials. *Chem Mater* 4 (1992), pp. 1395–1403.
- [31] T. Lan, P. D. Kaviratna, and T. J. Pinnavaia, On the Nature of Polyimide-Clay Hybrid Composites. *Chem. Mater.*, 6 (1994), pp 573.
- [32] P. B. Messersmith and E. P. Giannelis, Synthesis and barrier properties of poly(-caprolactone)-layered silicate nanocomposites. *J. Polym. Sci. Part A: Polym. Chem. Ed.*, 33 (1995), pp. 1407.
- [33] K. Masenelli-Varlot, E. Reynaud, G. Vigier, and J. Varlet, Mechanical properties of clay-reinforced polyamide. *J. Polymer. Sci., Part B: Polymer. Phys.*, 40 (2002), pp. 272.
- [34] K. Yano, A. Usuki, A. Okada, T. Kurauchi and O. Kamigaito, Synthesis and properties of polyimide–clay hybrid. *Polym Prepr (Jpn)* **32** 1 (1991), pp. 65–67.
- [35] T. Lan, P.D. Kaviratna and T.J. Pinnavaia, On the nature of polyimide–clay hybrid composites. *Chem Mater* 6 (1994), pp. 573–575.
- [36] K. Yano, A. Usuki and A. Okada. Synthesis and properties of polyimide–clay hybrid films. *J Polym Sci, Part A: Polym Chem* 35 (1997), pp. 2289–2294.
- [37] Z.-K. Zhu, Y. Yang, J. Yin, X.Y. Wang, Y.C. Ke and Z.N. Qi. Preparation and properties of organosoluble montmorillonite/polyimide hybrid materials. *J Appl Polym Sci* 73 (1999), p. 2063.
- [38] X. Huang, S. Lewis, W.J. Brittain and R.A. Vaia, Synthesis of polycarbonate-layered silicate nanocomposites via cyclic oligomers. *Macromolecules* 33 (2000), pp. 2000–2004.
- [39] M. Mitsunaga, Y. Ito, S. Sinha Ray, M. Okamoto and K. Hironaka, Polycarbonate/clay nanocomposites: nanostructure control and foam processing. *Macromol Mater Engng* 288 (2003), pp. 543–548.
- [40] A. Usuki, T. Mizutani, Y. Fukushima, M. Fujimoto, K. Fukumori, Y. Kojima, N. Sato, T. Kurauchi, and O. Kamigaito, U.S. Patent 4,889,885 (1989).
- [41] M. S. Wang and T. J. Pinnavaia, Clay-Polymer Nanocomposites Formed from Acidic Derivatives of Montmorillonite and an Epoxy Resin. *Chem Mater.* 6 (1994); pp 468.
- [42] T. Lan and T. J. Pinnavaia, Clay-Reinforced Epoxy Nanocomposites. *Chem. Mater.* 6 (1994); pp 2216.
- [43] T. Lan, P. J. Kaviratna, and T. J. Pinnavaia, Mechanism of Clay Tactoid Exfoliation in Epoxy-Clay Nanocomposites. *Chem. Mater.*, 7 (1995), pp.2214

- [44] P. Kelly, A. Akelah, S. Qutubuddin, and A. Moet, Synthesis and characterization of "epoxyphilic" montmorillonites. *J. Mater Sci.*, **29** (1994), pp. 2274.
- [45] Hu Y., Song L., Xu J. Y., Yang L., Chen Z. Y., Fan W.C., *Synthesis of polyurethane/clay intercalated nanocomposites*, Colloid Poly, Sci., Volume 279, 2001, Pages 819-822.
- [46] Song L., Hu Y., Li B.G., Chen Z. Y., Fan W.C., A study on the synthesis and properties of polyurethane/clay nanocomposites, *Int. J. Polym Anal. Ch.*, Volume 8, 2003, Pages 317-326.
- [47] Zerda A.S., Lesser A.J., Intercalated clay nanocomposites: morphology, mechanics, and fracture behavior, *J. Polym. Sci., Part B*, Volume 39, 2001, Pages 1137-1146.
- [48] Yasmin A., Abot J.L., Daniel I.M., Processing of clay/epoxy nanocomposites with a three-roll mill machine, *Mat. Res. Soc. Symp. Proc.*, Volume 740, 2003, Pages 75-80.
- [49] Yasmin A., Abot J.L., Daniel I.M., Processing of clay/epoxy nanocomposites by shear mixing, *Scripta Mat.*, Volume 49, 2003, Pages 81-86.
- [50] Yasmin A., Abot J.L., Daniel, I.M., Characterization of structure and mechanical behavior of clay/epoxy nanocomposites. San Diego: ICCM -14; 2003.
- [51] Luo J-J, Daniel I.M., Characterization and modeling of mechanical behavior of polymer/clay nanocomposites, *Comp. Sci. Tech.*, Volume 63, 2003, Pages 1607-1616
- [52] Wu C.L., Zhang M.Q., Rong M.Z., Friedrich K., *Tensile performance improvement of low nanoparticles filled-polypropylene composites*, Composites Science and Technology, Volume 62, 2002, Pages 1327-1340.
- [53] Sharma S.K., Nayak S.K., *Surface modified clay/polypropylene (PP) nanocomposites: Effect on physics-mechanical, thermal and morphological properties*, Polymer Degradation and Stability, Volume 94, 2009, Pages 132-138.
- [54] Galgali G., Agarwal S., Lele A., *Effect of clay orientation on the tensile modulus of polypropylene nanoclay composites*, Polymer, Volume 45, 2004, Pages 6059-6069.
- [55] Bureau M.N., Ton-That M., Perrin-Sarazin F., *Essential work of fracture and failure mechanism of polypropylene-clay nanocomposites*, Engineering Fracture Mechanics, Volume 73, 2006, Pages 2360-2374.

- [56] Drozdov A.D., Lejre A.H., Christiasen J., *Viscoelasticity, viscoplasticity, and creep failure of polypropylene/clay nanocomposites*, Composites Science and Technology, Volume 69, 2009, Pages 2596-2603.
- [57] Dong Y., Bhattacharyya D., *Effect of clay type, clay/compatibilizer content and matrix viscosity on the mechanical properties of polypropylene/organoclay nanocomposites*, Composites: Part A, Volume 39, 2008, Pages 1177-1191.
- [58] Santos K.S., Liberman S.A., Oviedo M.A.S., Mauler R.S., *Optimization of the mechanical properties of polypropylene-based nanocomposites via the addition of a combination of organoclays*, Composites: Part A, Volume 40, 2009, Pages 1199-1209.
- [59] Yasmin A., Luo J.J., Abot J.L., Daniel I.M., *Mechanical and thermal behavior of clay/epoxy nanocomposites*, Composites Science and Technology, Volume 66, 2006, Pages 2415-2422.
- [60] Sarathi R., Sahu R.K., Rajeshkumar P., *Understanding the thermal, mechanical and electrical properties of epoxy nanocomposites*, Materials Science and Engineering A., 2007, Pages 567-578.
- [61] Saber-Samandari S., Khatibi A.A., Basic D., *An experimental study on clay/epoxy nanocomposites produced in a centrifuge*, Composites: Part B Volume 38, 2007, Page 102-107.
- [62] Zhao Q., and Hoa S.V., Toughening mechanism of epoxy resins with micro/nano particles, Journal of Composites Materials, Vol 41, 2007, No:2.
- [63] Bayar S., *An Experimental and theoretical Study of the Effect of Temperature on The Mechanical Behavior of Nanoclay Reinforced Polymers*. PhD Dissertation, CUNY, NY, 2012.